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CATALYTIC WET AIR OXIDATION OF LINEAR ALKYLBENZENE SULPHONATE

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Abstract. In view of slow rates of wet air oxidation process, the catalytic oxidation of organic-containing wastewaters over various homogeneous and heterogeneous catalysts has received a lot of attention. The impact of heterogeneous catalysts on the Wet Air Oxidation (WAO) of Linear Alkylbenzene Sulphonate (LAS) has been determined. Experiments were carried out at temperatures from 180°C to 220°C for 120 minutes, and an oxygen partial pressure of 1.5MPa was maintained for all the experiments. The catalyst was introduced to the original solution of LAS and all of the catalysts were used in a powder form. WAO of LAS in the presence of heterogeneous catalysts increased the TOC and COD removals. $CuO.ZnO/Al_2O_3$ was found to be the effective catalyst for the degradation of LAS and this catalyst were capable of oxidising VFAs which were resistant to further oxidation during uncatalysed WAO. Desulphonation did occur in the presence of Pt/Al_2O_3 and $CuO.ZnO/Al_2O_3$. Leaching of both copper and zinc occurred during the $CuO.ZnO/Al_2O_3$ catalysed WAO. It was found that within the range of experimental conditions studied, the homogeneous activity of leached metals is insignificant and therefore, the role of heterogeneous activity of $CuO.ZnO/Al_2O_3$ is still dominant.

Key Words: Heterogeneous catalysts, Surfactants, WAO, TOC, COD.

1.0 INTRODUCTION

Linear alkylbenzene sulphonates (LAS) are the world's most widely used synthetic detergents in both household and industrial cleaning products. LAS contain an aromatic ring sulphonated at the para position and attached to a linear alkyl chain at any position except the terminal positions. The commercial product mainly consists of a complex mixture of various homologues and isomers representing different alkyl chain lengths (typically between 10 and 14 carbon atoms) and aromatic ring positions along the linear chain.

The linear alkyl chain is considered to be readily biodegradable which is why LAS is so widely used [1,2]. However, the biodegradation of many surfactants, including LAS, is inhibited at concentrations above 20–50 mg/L [3]. Even below these concentrations, LAS is still difficult to biodegrade because as much as a third of the LAS can be adsorbed and left untreated in the sludge in biological reactors [4]. At higher concentrations, such as those of detergent manufacturing wastewater streams which can reach values as high as 50000 mg/L COD, LAS is biorecalcitrant. These effluents are treated by flocculating the surfactant with

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lime and salts and landfilling the resulting sludge. This technique is not desirable though, since LAS is not remediated but rather is transferred from being a liquid contaminant to a sludge waste.

In search of efficient destructive treatment technologies for LAS-containing effluents, several chemical oxidation processes have been tested. Advanced oxidation processes such as ozonation [5,6], TiO_2 photocatalysis [7], the use of Fenton's reagent [8] and electrochemical treatment [9] have been employed to treat relatively dilute LAS solutions (i.e. in the order of 100 mg/L). Nonetheless, these processes cannot treat effectively the high concentrations of LAS typically found in industrial effluents. A suitable technology for the treatment of high-concentration LAS is wet air oxidation (WAO) since LAS is both water-soluble and soluble at appropriate concentrations in the industrial effluents of interest.

In related previous studies, several researchers have employed uncatalysed WAO to treat LAS solutions with initial concentrations up to 1600 mg/L. Emphasis was given on the effect of operating conditions such as temperature, pressure and solution pH on degradation kinetics, pathways and mechanisms [10–12] as well as on developing a combined treatment scheme comprising WAO and aerobic biodegradation [13]. These studies have shown that uncatalysed WAO at temperatures up to 240^{o}C and prolonged treatment times up to 390 min was needed to completely remove active detergency and convert LAS to various intermediate compounds; however, further oxidation of these intermediates proved difficult and complete mineralisation could not be achieved. In view of this, the use of suitable catalysts could possibly promote WAO at milder operating conditions and shorter treatment times as several catalytic WAO processes for industrial wastewater treatment are known to exist [14]. However, no information regarding the catalytic WAO of LAS is available in the literature.

The aim of this work is to study the treatment of synthetic aqueous solutions containing a commercial LAS, namely sodium dodecylbenzene sulphonate (SDBS), by means of catalytic WAO and ultrasound irradiation. The catalytic activity of four heterogeneous catalysts (i.e. a mixed copper–zinc oxide and three noble metals, namely platinum, palladium and ruthenium) to wet oxidise SDBS is evaluated; catalyst selection was based on our previous experience concerning the WAO of agro-industrial [15] and non-ionic polymer processing [16] effluents.

2.0 EXPERIMENTAL

2.1 Wet Air Oxidation Experiments

A 600-mL high pressure reactor (Air Products PLC) is capable of performing semibatch or continuous experiments at pressure up to 10 MPa and temperatures up to 300°C. A schematic diagram of the reactor system is shown in Figure 1. In a typical semi-batch run, 500 mL (with the headspace of 100 mL) of the LAS solution was batch loaded into the reactor. The reactor was then heated up to the operating temperature under nitrogen. Experiments were carried out at temperatures from 180°C to 220°C, and an oxygen partial pressure of 1.5 MPa was maintained for all the experiments. As soon as the operating temperature was reached, air was continuously fed into the reactor (through V1, V2, V3 and V12) while being stirred at 1000 rpm to start the reaction ensuring good mass transfer from the gas to the liquid phase. The system was also equipped with a bursting disk to vent the reactor contents in the case of reactor overpressure.

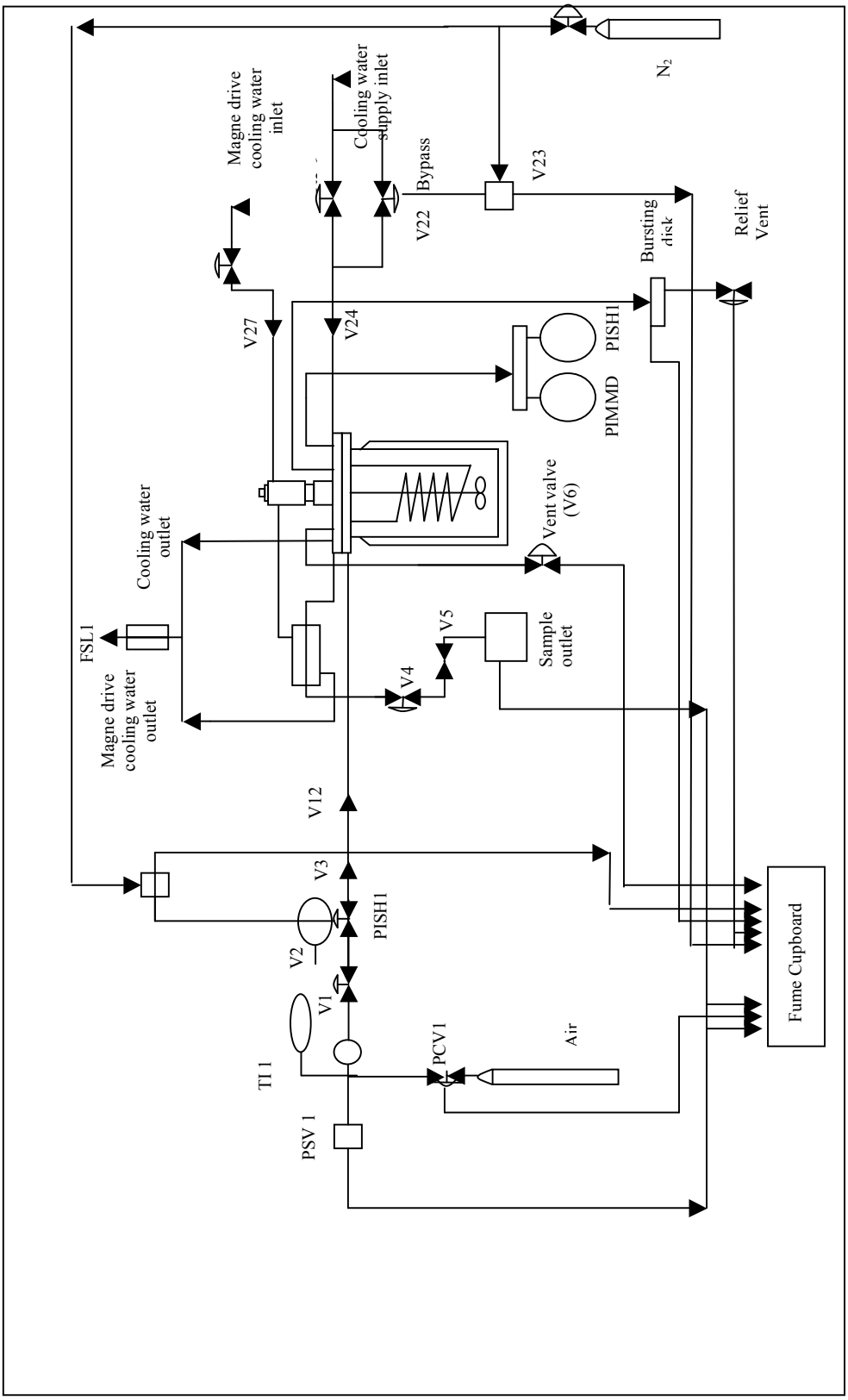


Figure 1 The schematic diagram of UMIST reactor system

For the catalytic experiments, the catalyst was introduced to the original solution of LAS and all of the catalysts were used in a powder form. Special attention was given to the liquid sampling procedure. To prevent the contamination of the samples, the sample pipe (through V4 and V5) was flushed with a small amount of sample while V1 was shut-off, before the samples were periodically withdrawn (30, 60 and 90 min) from the sample cabinet. For those experiments in which relatively small liquid volumes were required for further analysis (e.g. for TOC, COD measurements, High Performance Liquid Chromatography (HPLC) analysis and leaching of copper, zinc and aluminum), 25-30 mL were withdrawn from the sample cabinet (through V4 and V5). For those experiments in which a final (after 120 min oxidation) liquid sample was needed, the reaction vessel contents were collected at the end of each run. Samples that were collected were immediately analysed or refrigerated. To minimise the extent of reaction time, the following procedure was utilised. When the final reaction time had been reached (120 min), the air was shut-off and the vessel was depressurised (through vent valve) to remove most of the air from the reactor and to stop the reaction. To decrease the length of cooling time, water was supplied to the reactor through V24 and V26. As soon as the temperature dropped to ambient temperature, the vessel was opened and its contents were collected for further analysis.

2.2 Catalysts

The following heterogeneous catalysts, were used in this study. (a) A metal oxide comprising 59% w/w CuO, 31.7% w/w ZnO and 9.3 w/w Al_2O_3. The catalyst was supplied by ICI Katalco, UK. (b) Three noble metal catalysts, namely: platinum (Pt), palladium (Pd) and ruthenium (Ru) with a noble metal loading of 5% w/w supported on alumina (Aldrich, UK). All catalysts were characterized with respect to their BET surface area by nitrogen adsorption; these were 98, 144, 100 and 150m^2/g for $CuO.ZnO/Al_2O_3$, Pt/Al_2O_3, Pd/Al_2O_3 and Ru/Al_2O_3, respectively. For those WAO experiments carried out in the presence of copper and zinc ions, the appropriate amounts of $Cu(NO_3)_2.3H_2O$ (BDH, UK) and $Zn(NO_3)_2.6H_2O$ (Aldrich, UK) were dissolved in the solution to give a metal concentration of 10 and 15 mg/L respectively.

2.3 Analysis of TOC and COD

Total organic carbon (TOC) was measured with a Shimadzu 5050 TOC Analyser whose operation is based on combustion/non-dispersive infrared (NDIR) gas analysis. Total carbon was measured first followed by inorganic carbon and TOC was determined by subtracting inorganic from total carbon. The uncertainty in this assay, quoted as the standard deviation of three separate measurements, was never larger than 1% for the range of TOC concentrations under consideration. Chemical oxygen demand (COD) was determined by the dichromate method. The appropriate amount of sample was introduced into a commercially available digestion solution (Hach Europe, Belgium) containing sulphuric acid, mercuric sulphate and chromic acid. The mixture was then refluxed for 120 min at 150°C in a COD Reactor, (Model 45600-Hach Company, USA). After cooling, the COD concentration was measured colorimetrically using a DR/890 colorimeter (Camlab, UK). The average value of three separate measurements per vial was taken and the deviations never exceeded 3% for the range of COD concentrations measured.

2.4 Determination of SDBS Concentration

The concentration of SDBS subject to WAO was followed using high performance liquid chromatography (HPLC) on a Varian ProStar HPLC equipped with photodiode array detector. A gradient method utilizing an acetonitrile:water (buffered with sodium

perchlorate) mobile phase at a flow rate of 1 mL/min and ambient temperature with an injection volume of 100 μl was used to elute and separate SDBS on a reverse phase C18 ThermoHypersil column. Two mobile phases were used as follows: solution A containing acetonitrile:water (70:30) and 0.15 M sodium perchlorate, and solution B containing 0.15M sodium perchlorate in water. Details of the gradient method used are given elsewhere [10]. The chromatograms were analysed using the Star Chromatography Workstation Version 6.

2.5 Determination of Volatile Fatty Acids (VFAs) Concentration

The concentration of VFAs produced during WAO experiments was followed by means of gas chromatography (GC). GC analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph using a 10 m x 0.53 mm, 1.0 μm film thickness column (Phase Separation Ltd., UK). Helium was used as the carrier gas at 1.2 mL/min flowrate and the injection volume was 2 μL. The chromatograms were processed using HP Chemstation software.

2.6 Determination of Leached Metals Concentration

Catalyst leaching is vital for three reasons [12]: (i) An additional treatment step such as precipitation, may be necessary to remove any leached catalyst from the treated effluent especially if a further biological treatment process is to be used (ii) Continuous leaching would lead progressively to the deactivation of the heterogeneous catalyst and (iii) Since homogeneous catalysts i.e. Cu^{2+}, are known to be effective catalysts for liquid-phase oxidation, dissolved metal may be responsible for homogeneous catalysed reactions and a homogeneous-heterogeneous reaction system should be considered rather than a purely heterogeneous reaction system.

Leaching of $CuO.ZnO/Al_2O_3$ catalyst in the reaction mixture subject to WAO was assessed by measuring the concentration of dissolved metal components with atomic absorption (Atomic Absorption Analyser-Model SpectrAA-10, Varian, UK). 1000 mg/L atomic absorption standard solutions of the metals under consideration were provided (Aldrich, UK) and diluted to various concentrations with deionised water. Leaching of noble metal catalysts was measured using inductively coupled plasma-optical emission spectrophotometry (ICP-OES) (Varian-Vista MPX Axial CCD-simultaneous ICP-OES). Wavelengths of 214.4, 340.5 and 267.9 nm were used for Pt, Pd and Ru analysis respectively.

3.0 RESULTS AND DISCUSSION

3.1 Catalytic Wet Air Oxidation of SDBS

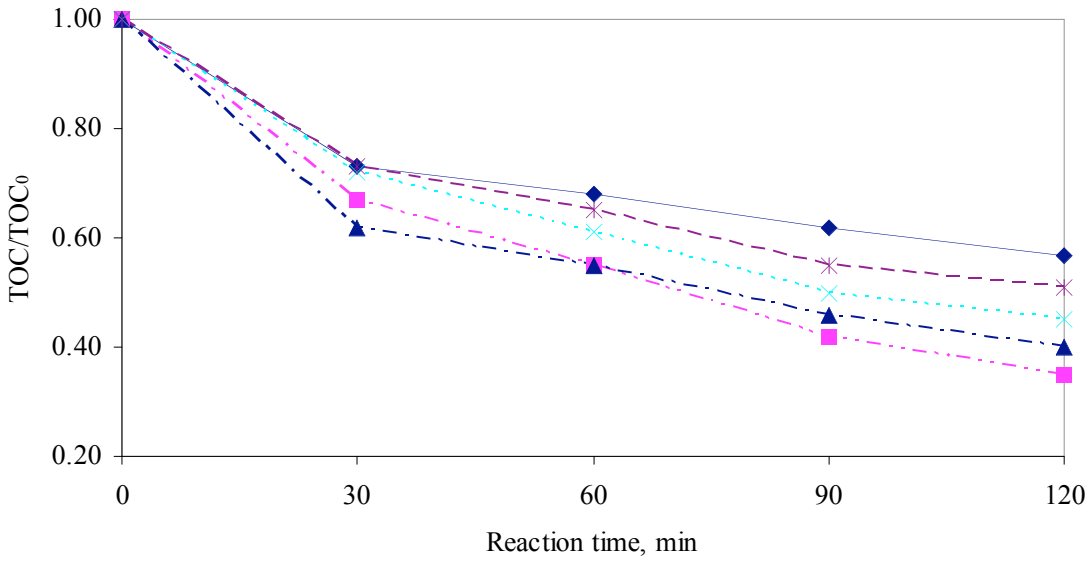
LAS with an initial concentration of 1000 mg/L (TOC ≈ 590 mg/L, COD ≈ 1900 mg/L) was reacted at 180 °C, 200 °C and 220 °C for 120 min at an oxygen partial pressure of 1.5 MPa. Figures 2–4 show the effect of reaction temperature on TOC and COD concentration-time profiles during oxidation with various catalysts, while the corresponding uncatalysed run is given as a reference. As seen, the catalytic conversion of both TOC and COD is faster than the uncatalysed one and also increases with increasing temperature. Of the various catalysts tested, $CuO.ZnO/Al_2O_3$ was more effective than noble metals leading to 65 %, 70 % and 77 % TOC reduction after 120 min at 180, 200 and 220°C respectively; the corresponding values of COD reduction were 72%, 76% and 77% , respectively. Of the noble metals used, Pt/Al_2O_3 and Ru/Al_2O_3 appeared to be the most and least active oxidation catalysts respectively.

It can be seen that TOC and COD were not completely destroyed, indicating the presence of refractory organic compounds in the reaction mixture. The residual organic content is only partly due to unreacted SDBS; as seen in Table 1, SDBS is rapidly oxidised and in all cases, more than 83% conversion can be achieved after 90 min of oxidation. It is well established that the wet oxidation of several classes of organics typically proceeds through the formation of various intermediate compounds which are further oxidised to form short-chain volatile fatty acids (VFAs) and other organic acids [14,16]. Compounds such as formic, acetic and propionic acids are very resistant to total oxidation even under harsh conditions and their oxidation to carbon dioxide is usually the rate-determining step in most WAO processes [17,18].

In related studies by Mantzavinos and colleagues, they found that the primary reaction pathways and mechanisms occurring during LAS uncatalysed WAO were elucidated [10,12]. It was found that LAS could be easily oxidised to yield sulphonated aromatic intermediates with short alkyl chains, while the segments of alkyl chains broken off the intermediates appeared as short acids such as formic, acetic, propionic, butanoic and succinic acids. In parallel, considerable amounts of sulfate present in the reaction mixture indicated that desulfonation of LAS and its sulphonated intermediates had occurred. Figure 5 shows the pH change during SDBS oxidation at 180°C, while similar profiles were obtained for the experiments carried out at the other two temperatures. In all cases, as pH was left uncontrolled during the reaction, it rapidly dropped from its initial value of 8 to about 3.5 within the first 30–60 min and remained practically unchanged thereafter, thus implying the presence of acidic compounds.

Table 1 SDBS conversion (%) for various wet Air oxidation conditions

Conditions	No Catalyst	Ru/Al_2O_3	Pd/Al_2O_3	Pt/Al_2O_3	$CuO.ZnO/Al_2O_3$
180°C; 30 min	59	59	64	65	81
200°C; 30 min	76	77	80	82	89
220°C; 30 min	86	86	87	89	95
180°C; 90 min	83	83	87	90	94
200°C; 90 min	87	87	87	89	98
220°C; 30 min	99.6	99.7	99.7	99.8	99.9



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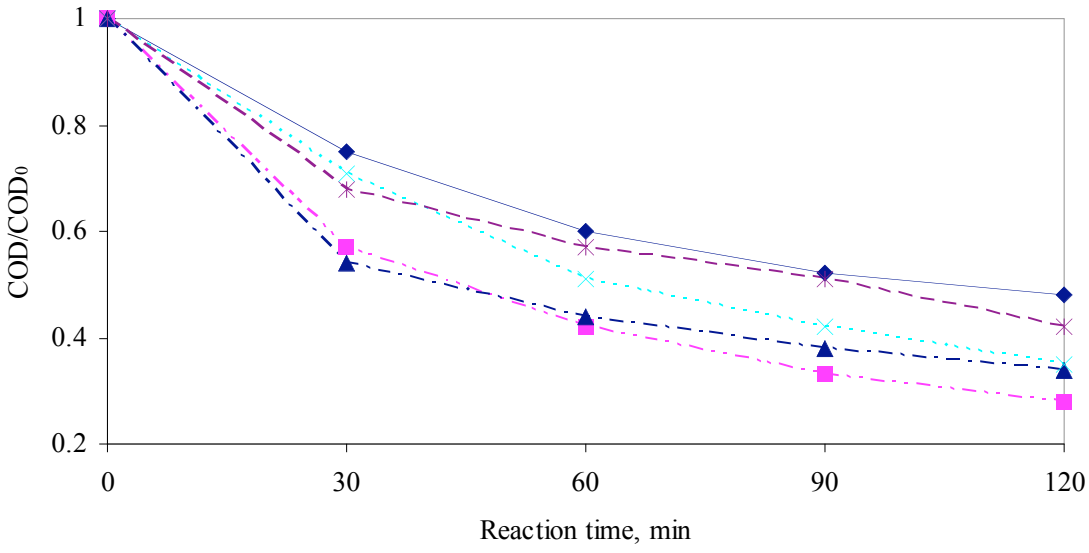

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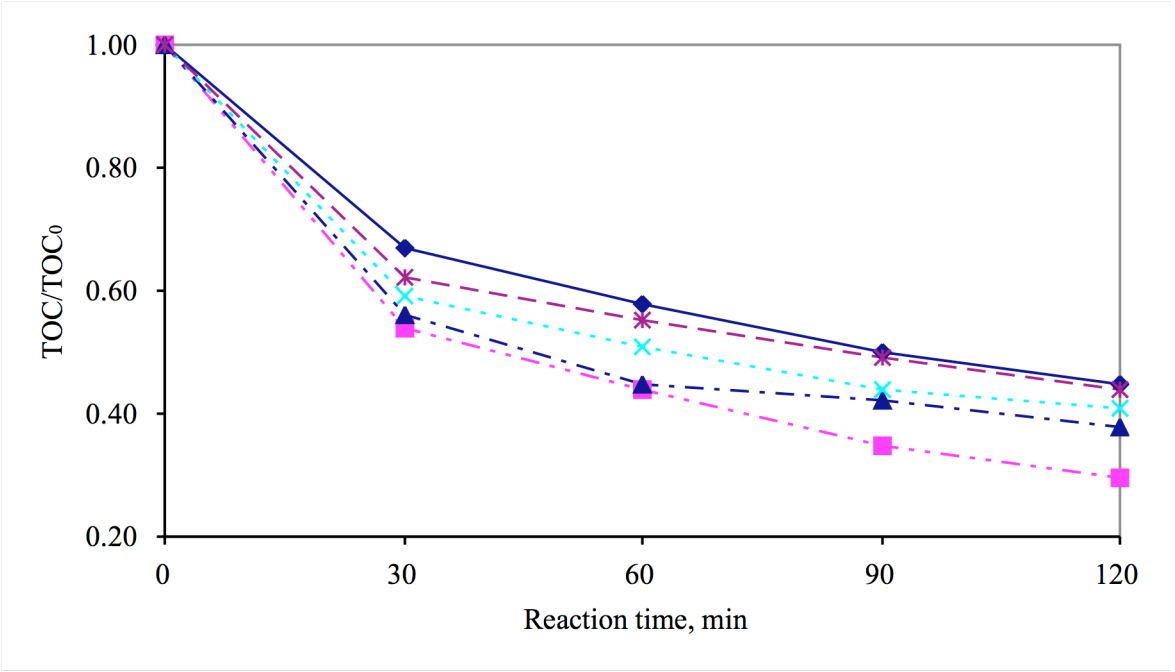
Figure 2 Concentration-time profile of (a) TOC and (b) COD during the wet air oxidation of SDBS at 180°C. -◆- Uncatalysed, -*-Ru/Al_2O_3, -x- Pd/Al_2O_3, -▲- Pt/Al_2O_3, -■- $CuO.ZnO/Al_2O_3$



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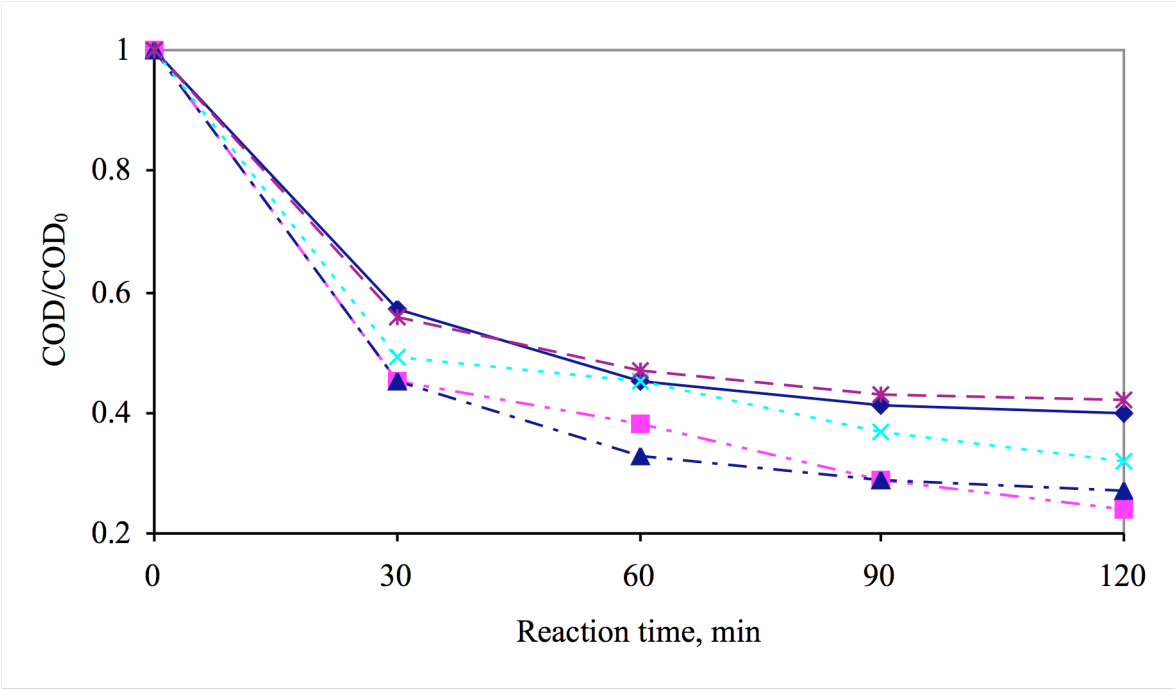

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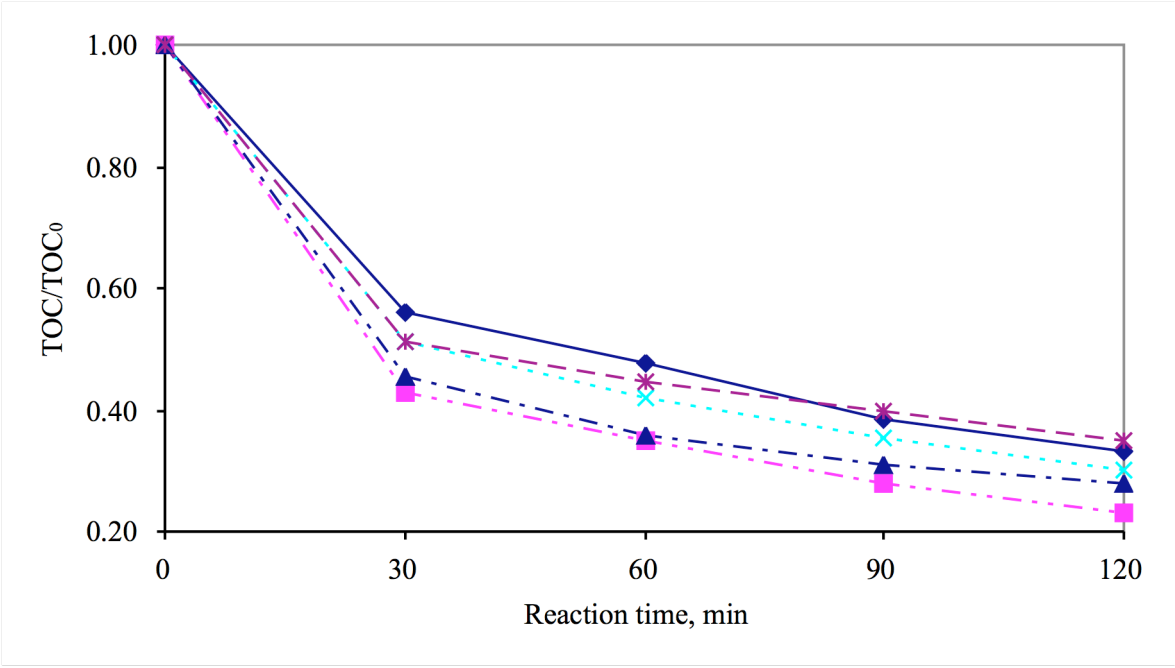
Figure 3 Concentration-time profile of (a) TOC and (b) COD during the wet air oxidation of SDBS at 200°C. -◆- Uncatalysed, -*-Ru/Al_2O_3, -x- Pd/Al_2O_3, -▲- Pt/Al_2O_3, -■- $CuO.ZnO/Al_2O_3$



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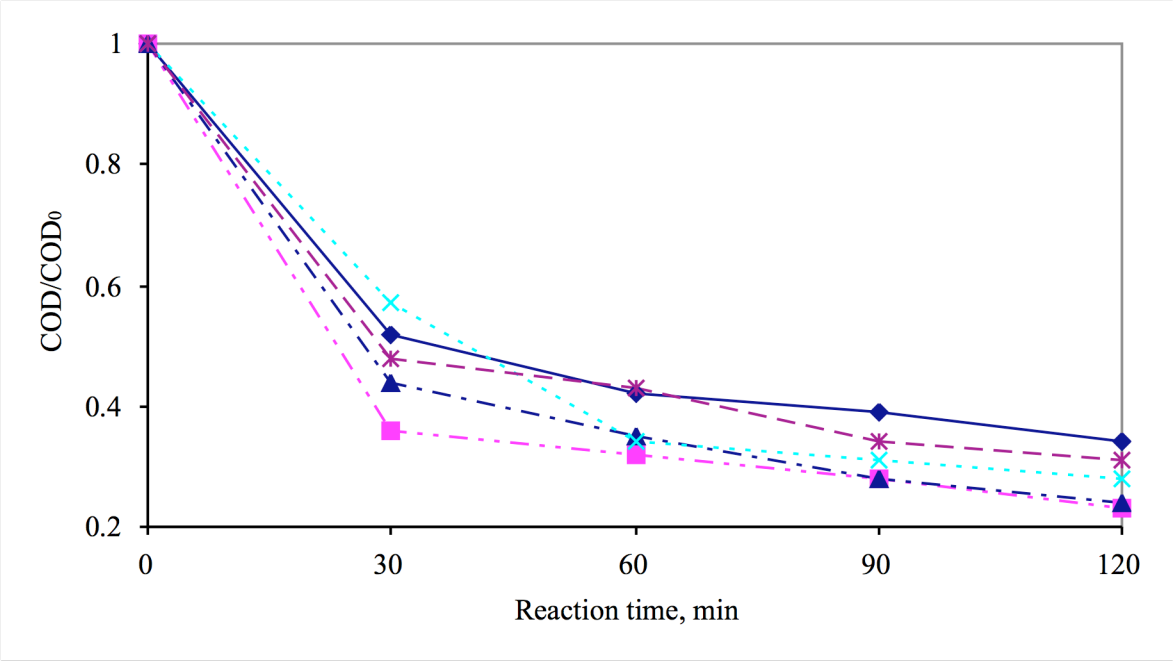


(b)

Figure 4 Concentration-time profile of (a) TOC and (b) COD during the wet air oxidation of SDBS at 220°C. -◆- Uncatalysed, -*-Ru/Al_2O_3, -x- Pd/Al_2O_3, -▲- Pt/Al_2O_3, -■- $CuO.ZnO/Al_2O_3$

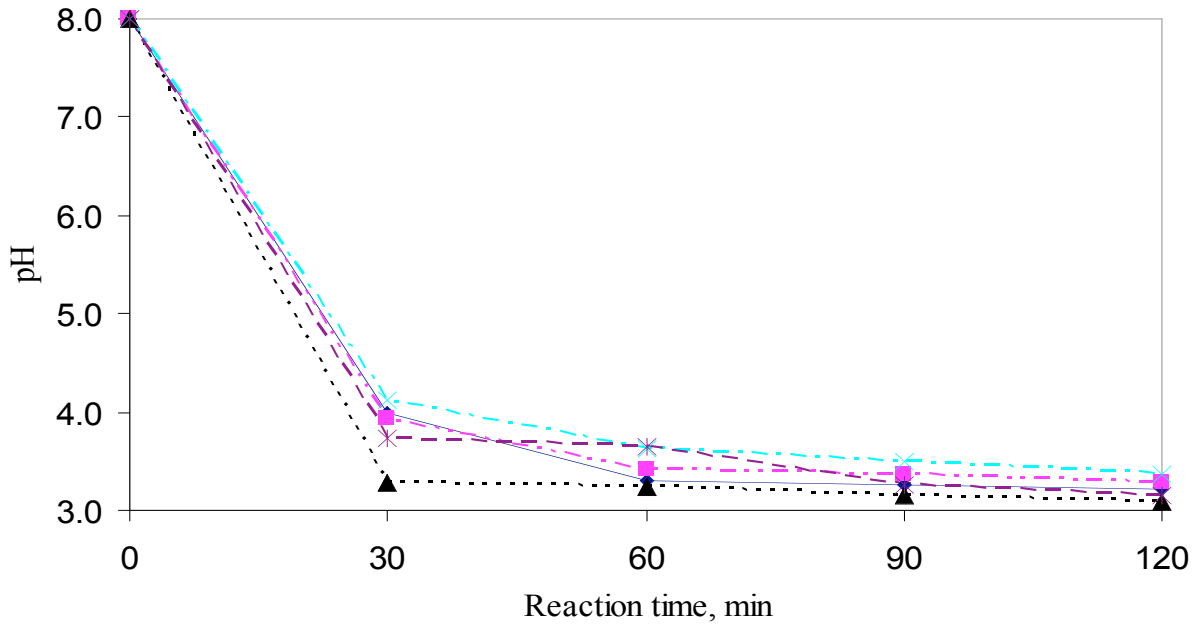


Figure 5 pH change during the wet air oxidation of SDBS at 180°C. -◆- Uncatalysed, -*- Ru/Al_2O_3, -x- Pd/Al_2O_3, -▲- Pt/Al_2O_3, -■- $CuO.ZnO/Al_2O_3$

3.2 Gas Chromatograph Analysis

GC analysis verified the formation of several VFAs with acetic and propionic acids being the dominant ones in terms of concentration. Table 2 shows their concentration in the reaction mixture after 120 min of oxidation at various conditions. As seen, acid concentration increases with increasing temperature and also depends on the catalyst used; these results are consistent with those shown in Figures 2–4 and Table 1 regarding the effect of temperature on conversion as well as the relative catalytic activity. For the experiment with $CuO.ZnO/Al_2O_3$ and the respective uncatalysed one, the concentrations of acetic and propionic acids were followed throughout the reaction and the results are shown in Figure 6. It should be pointed out that concentration data are presented as the ratio of organic carbon concentration calculated from the measured acid concentration to the total TOC for every sample. Figure 6a clearly shows that the rate of acetic acid accumulation in the reaction mixture (i.e. the difference between its formation and degradation rates) is far greater than that of other intermediate compounds.

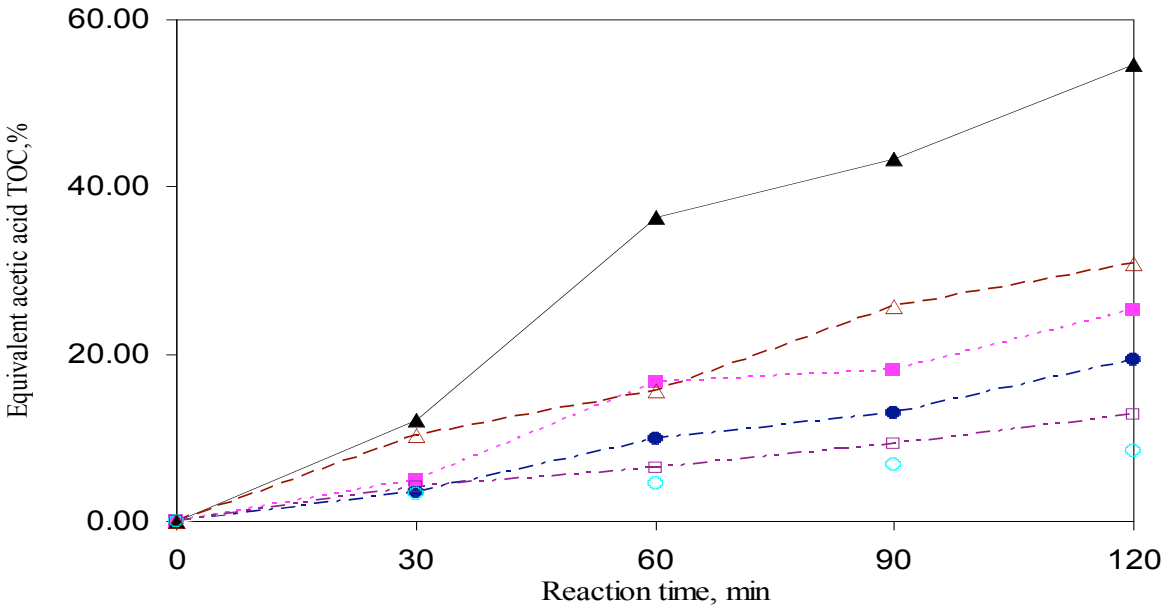
Table 2 Concentration (mg/L) of acetic acid (AA) and propionic acid (PA) after 120 min of SDBS wet air oxidation at various temperatures

Conditions	No Catalyst	Ru/Al_2O_3	Pd/Al_2O_3	Pt/Al_2O_3	$CuO.ZnO/Al_2O_3$
AA; 180°C	72.3	74.1	78.2	88	101.6
AA; 200°C	86.2	90.3	94.8	102.7	113.8
AA; 220°C	152.8	160.1	168	181.9	200.3
PA; 180°C	17	17.5	18.9	20.7	23.9
PA; 200°C	20.3	21.5	23.5	25	28.6
PA; 220°C	36	39.5	42	46.9	52.8

In all cases, acetic acid concentration constantly increases with reaction time, while at the same time TOC decreases, thus resulting in the profiles shown in Figure 6a. This is more pronounced for the catalytic experiment where acetic acid accounts for over 50% of the residual TOC after 120 min of oxidation at 220°C. On the other hand, propionic acid concentration (as shown in Figure 6b) reaches a maximum during catalytic oxidation and then begins to decrease as $CuO.ZnO/Al_2O_3$ is capable of catalyzing its degradation to compounds such as acetic and formic acids [17]. This is consistent with previous studies showing that propionic acid, despite being a refractory compound at temperatures as high as about 250°C, is still more easily destroyed during WAO than acetic acid [18].

3.3 Catalysts Leaching

Since $CuO.ZnO/Al_2O_3$ heterogeneous catalyst was found to be, in general, more effective (in terms of TOC and COD removals) than noble metal catalysts in oxidising LAS, further experiments have been performed to test the leaching of a $CuO.ZnO/Al_2O_3$ catalyst. The stability of the $CuO.ZnO/Al_2O_3$ catalyst was studied with respect to metal leaching. Leaching was verified by measuring the concentration of dissolved metals in the solution subject to oxidation with $CuO.ZnO/Al_2O_3$. At 200°C, 120 min reaction time, final pH value of 3, both copper and zinc leached at concentrations of about 10 mg/L, while aluminium did not leach at a measurable concentration. These findings are consistent with those reported elsewhere [19] regarding the stability of a $CuO.ZnO/Al_2O_3$ catalyst used for the catalytic WAO of agro-industrial effluents. Copper and zinc were found to leach at acidic or even neutral conditions (i.e. in the pH range 3.5–7) with the extent of leaching increasing with decreasing pH and increasing oxidation temperature. Samples subject to oxidation with noble metals were also analysed with respect to the dissolved metal concentration. In all cases, catalyst leaching did not occur to a measurable extent with metal concentration always below the detection limit of the ICP technique.



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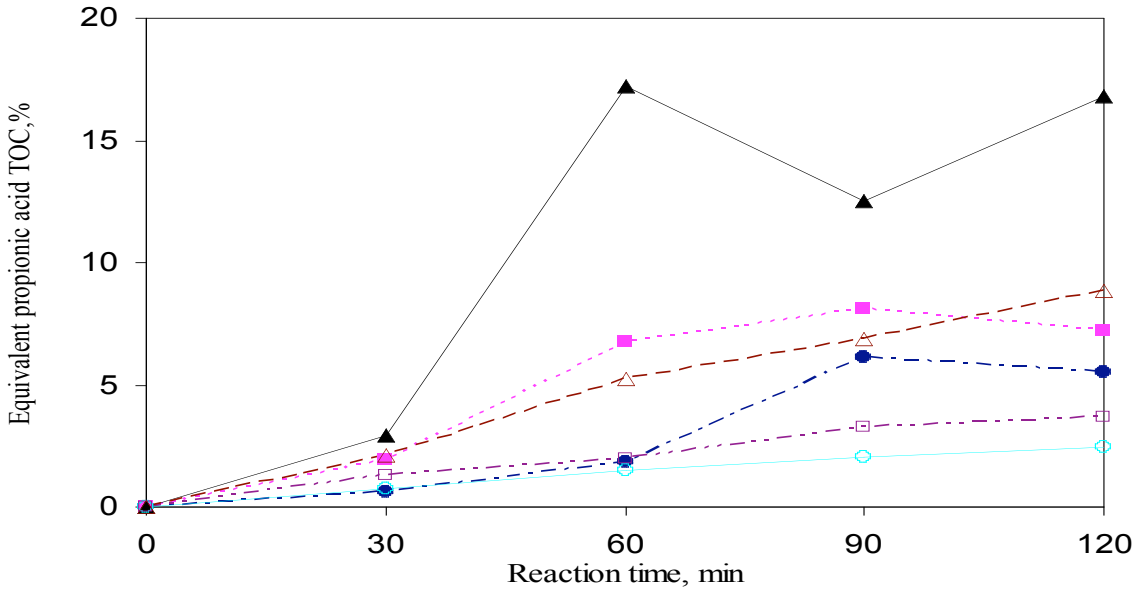

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Figure 6 Concentration-time profile of (a) acetic acid and (b) propionic acid during the wet air oxidation of SDBS at various temperatures. -o-, -•-180°C; -□-, -□-,200°C; -Δ-, -▲-, 220°C. Open symbols: Uncatalysed; Closed symbols: $CuO.ZnO/Al_2O_3$.

Since homogeneous catalysts, e.g. Cu^{2+}, are effective oxidation catalysts, dissolved metals must be responsible for homogeneously catalysed reactions and a homogeneous–heterogeneous reaction system should be considered rather than a purely heterogeneous reaction. To estimate the impact of dissolved metals on SDBS degradation, an additional experiment was carried out at 200°C using 10 mg/L of Cu^{2+} and 15 mg/L Zn^{2+} together as catalysts, thus simulating the leaching conditions in the run with $CuO.ZnO/Al_2O_3$. This experiment showed that the COD-time profiles were only marginally different from those obtained in the respective uncatalysed run; this suggests that, at the conditions studied, the homogeneous activity is insignificant and the role of heterogeneous activity is still dominant.

4.0 CONCLUSIONS

The catalytic wet air oxidation (CWAO) of LAS has been investigated using metal oxides and various noble metal catalysts, and the results have then been compared. In general, WAO in the presence of catalysts increase the overall degradation of LAS. Generally, $CuO.ZnO/Al_2O_3$ was found to be the effective catalysts for the degradation of LAS. Even though the relative catalytic activity for $CuO.ZnO/Al_2O_3$ was lower than those noble metal catalysts ($CuO.ZnO/Al_2O_3$ the ratio was 1.96×10^3 m^2m^{-3}, and for Pt/Al_2O_3, Pd/Al_2O_3 and Ru/Al_2O_3 are 2.88×10^3 m^2m^{-3}, 2.0×10^3 m^2m^{-3} and 3.0×10^3 m^2m^{-3} respectively), $CuO.ZnO/Al_2O_3$ was found to be capable of oxidising compounds, such as propionic and acetic acids, which were found to be resistant to oxidation during both uncatalysed and noble metal (except Pt/Al_2O_3) catalysed runs. Furthermore, $CuO.ZnO/Al_2O_3$ also catalyses the oxidation of both alkyl chain and sulphonated aromatics (i.e. 4-sulphobenzoic acid) that was refractory for further oxidation in both uncatalysed and noble metal catalysed WAO.

Consequently, $CuO.ZnO/Al_2O_3$ catalysed WAO gave the largest destruction of TOC and COD of all the WAO treatments studied.

Although $CuO.ZnO/Al_2O_3$ resulted in the largest destruction of TOC and COD than those noble metal catalysed WAO, leaching of both copper and zinc occurred during the $CuO.ZnO/Al_2O_3$ catalysed WAO. The effect of homogeneous ions resulting from such leaching on the COD removals, have been quantified. It was noticed that within the range of experimental conditions studied, the homogeneous activity of leached metals is insignificant and therefore, the role of heterogeneous activity of $CuO.ZnO/Al_2O_3$ is still dominant.

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